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# Synthesis and characterization of wollastonite glass–ceramics for dental implant applications

Selma A. Saadaldin[a,b], Amin S. Rizkalla[a,b,c,*]

[a] Medical Biophysics Department, Schulich School of Medicine & Dentistry, Western University, London, ON, Canada
[b] Schulich Dentistry, Schulich School of Medicine & Dentistry, Western University, London, ON, Canada
[c] Chemical and Biochemical Engineering, Faculty of Engineering, Western University, London, ON, Canada

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ABSTRACT

*Objectives.* To synthesize a glass–ceramic (GC) that is suitable for non-metallic one-piece dental implant application.

*Methods.* Three glasses in a $SiO_2$–$Al_2O_3$–CaO–$CaF_2$–$K_2O$–$B_2O_3$–$P_2O_5$–$CeO_2$–$Y_2O_3$ system were produced by wet chemistry. Differential thermal analysis (DTA) was carried out to determine the glass crystallization kinetic parameters and the heating schedules that were used for sintering of GCs. Crystalline phases and crystal morphologies were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Mechanical properties of the GCs were determined by ultrasonic and indentation tests and its machinability were evaluated. Chemical durability was carried out according to ISO 6872, whereas testing chemical degradation in tris buffered solution was executed according to ISO 10993-14.

*Results.* XRD of the GC specimens showed that wollastonite was the main crystalline with other secondary phases; GC2 had cristobalite as an additional phase. SEM of the GCs revealed dense acicular interlocking crystals. Young's modulus of elasticity ($E$), true hardness ($H_o$) and fracture toughness ($K_{IC}$) of the GCs were 89–100 GPa, 4.85–5.17 GPa and 4.62–5.58 MPa $m^{0.5}$, respectively. All GCs were demonstrated excellent machinability. The GCs exhibited various chemical durability and degradation rates. $K_{IC}$ values of the GCs following chemical durability testing were not significantly different from those of the original materials ($p > 0.05$). GC2 exhibited significantly higher $K_{IC}$ value compared with GC1 and GC3 ($p < 0.05$) and its chemical durability satisfied ISO 6872 specification for dental ceramics.

*Significance.* Wollastonite–cristobalite GC can be considered as a promising material for one-piece dental implant applications due to its strength, machinability and chemical durability.



## 1. Introduction

Glass–ceramics are polycrystalline materials with an inorganic–inorganic microstructure that were prepared from base glass by controlled crystallization. This was achieved by subjecting glasses to regulated heat treatment, which resulted in the nucleation and growth of one or more crystal phases within the glass. GCs have diverse physical, chemical, mechanical, optical and biological properties that can be modified with glass composition and heat treatment conditions [1]. As a consequence of the continuous need of the general public

* *Corresponding author at*: The University of Western Ontario, Dentistry, Schulich School of Medicine & Dentistry, London, ON, Canada N6A 5C1. Tel.: +1 519 661 2111x82212x86086; fax: +1 519 661 3416.
E-mail address: arizkalla@eng.uwo.ca (A.S. Rizkalla).

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as well as the dental professionals to eliminate dental metal-based products, there is a trend toward GCs and ceramic-based materials in the biomedical field [2]. Yttrium-stabilized tetragonal zirconia polycrystalline has been used extensively as a material of choice for ball heads in total hip replacement since the 1980s, and it became commercially available as non-metallic dental implants in the 2000s, owing to its strength, fracture resistance and appropriate optical properties [3]. However, zirconia undergoes aging through low-temperature degradation phenomenon that is moisture/water related and unfavorably affects its physical properties. In 2000, several hundreds of hip prosthesis failed over a short period of time. These failures were ascribed to an accelerated aging of the zirconia femoral head in particular batches [4]. Additionally, literatures showed that zirconia is correlated with two types of radiation impurities, alpha and gamma. Alpha radiation has been observed in a significant amounts and it could harm soft and hard tissues' cell due to their high ionization [5,6].

The wollastonites ($CaSiO_3$) are white glassy silicate minerals that occur as masses or tabular crystals of metamorphosed limestone. A silica chain GC that contains crystalline apatite and β-wollastonite (AW) was introduced in an $MgO–CaO–SiO_2–P_2O_5$ glassy matrix and it showed an excellent bioactivity, biocompatibility, machinability and adequate mechanical properties such as Young's modulus (117 GPa), compressive strength (1080 MPa), and bending strength (215 MPa) [7]. AW has been used for orthopedic applications—artificial vertebrae, intervertebral discs and iliac crest prostheses [7,8]. Kokubo proved that the mechanical strength of the AW was significantly unaffected in simulated body fluid at 36.5 °C and presumed that it can withstand a bending stress of 65 MPa in the human body environment for over 10 years [7]. Yet, the fracture toughness of the AW had relatively low values (2–2.5 MPa $m^{0.5}$); therefore it's limited to non-load bearing applications; and we note that, a custom AW prostheses production by conventional lost wax casting can be difficult as a result of the surface crystallization [7]. However, because of its excellent bioactivity, AW was used as a coating on different substrates such as titanium alloys [9] or as a composite scaffold by incorporation of AW with other materials [10,11].

Fracture toughness ($K_{IC}$) measures the resistance of a material to cracks propagation and the ability to prevent the initiation of catastrophic fracture. Indentation test has been considered as an accurate procedure to measure the fracture toughness for brittle materials, like ceramics and GCs. The indentation method has the advantages of simplicity and economy; where only small specimen area is needed, hence the technique is suited for comparative evaluation [12].

Chemical durability affects the clinical performance of dental materials. With a wide range of pH and temperature, dental materials should resist chemical degradation and dissolution. Chemical degradation of ceramic dental materials could lead to structure's weakening and surface roughness as a result of surface–ion exchange. This phenomenon leads to increase plaque attachment onto the biomaterials and intensify abrasion potential against opposing natural teeth and other restorative materials [13].

The brittle behavior of the GCs makes them sensitive to milling and machining; therefore, the development of machinable GCs for dental implant applications is considered a significant progress. A machinable dental implant material can be introduced to CAD–CAM technology and customized implants for different clinical cases can be fabricated, in addition to the possibility of the modification and adjusting of the implant at the time of surgical insertion. Machinable GCs can be used as one-piece dental implants where the upper part can be prepared to produce the abutment unit and get rid of multiple component implants i.e. fixture, screw and abutment.

The objectives of this study were to synthesize machinable wollastonite GCs with mechanical properties suitable for dental implant applications, to assess their chemical durability using acetic acid and tris buffered solution at different time points and evaluate their fracture toughness following chemical degradation testing.

**Table 1 – Chemical composition of the experimental glasses.**

| Glass component | Composition (wt%) | | |
|---|---|---|---|
| | G1 | G2 | G3 |
| $SiO_2$ | 55 | 59 | 50 |
| $Al_2O_3$ | 2 | 1 | 2 |
| CaO | 17 | 15 | 20 |
| $CaF_2$ | 12 | 12 | 12 |
| $K_2O$ | 5 | 5 | 7 |
| $B_2O_3$ | 3 | 3 | 3 |
| $P_2O_5$ | 1.5 | 2 | 3 |
| $CeO_2$ | 1.5 | – | – |
| $Y_2O_3$ | 3 | 3 | 3 |

## 2. Material and methods

### 2.1. Glass synthesis

Transparent glass frits were synthesized by wet chemical methods through four steps. In the beginning, the desired glass compositions in wt% (Table 1) were prepared by mixing batch ingredients {$Si(C_2H_5O)_4$, $Al(NO_3)_3{\cdot}9H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $CaF_2$, $KNO_3$, $H_3BO_3$, $Ce(NO_3)_3{\cdot}6H_2O$ and $Y(NO_3){\cdot}6H_2O$} in aqueous solution, and kept stirred overnight to commence hydrolysis and polycondensation of metal alkoxides. This was followed by spray-drying of the solutions at a feed flow rate of 10 ml/min, inlet air temperature of 160 °C and outlet air temperature of 80 °C using a 190 mini spray-dryer (BÜCHI, Switzerland). The spray-dried powders were calcined by means of a Ney 650 vacuum oven (Ney-Barkmeyer, USA) through sequential heating schedules at 200, 500 and 700 °C for 2 h. Finally, the calcined powders were melted in an uncovered platinum crucible at 1350 °C for 3 h in a high temperature furnace (Thermolyne Corporation, USA), followed by quenching in iced-water to obtain the glass frits.

### 2.2. Differential thermal analysis

Crystallization kinetic parameters of the glasses (G) were determined using SDT Q600 V20.5 Build 15 (TA Instruments, USA) at different five heating rates (10–50 °C/min), starting from room temperature up to 1200 °C under air atmosphere; for each heating rate, three-independent runs were carried